Headquarters U.S. Air Force

Integrity - Service - Excellence

Section 2
Lines of Evidence Used to Evaluate Natural Attenuation

U.S. AIR FORCE

Presented by

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Weight of Evidence

- **Independent and Converging Lines of Evidence Should be Used to Document and Quantify Natural Attenuation**

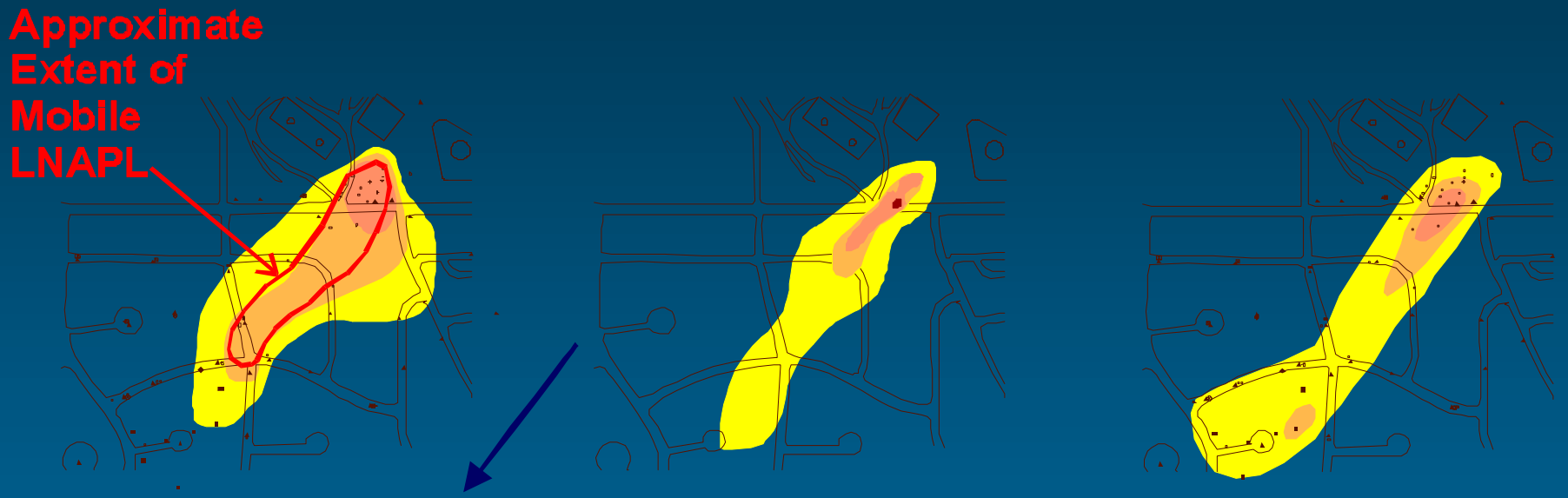
Lines of Evidence Used To Evaluate Natural Attenuation

1) Historical Database Showing Plume Stabilization and/or Loss of Contaminant Mass Over Time
2) Contaminant and Geochemical Analytical Data Showing Biodegradation
3) Microbiological Laboratory Data
4) Models???

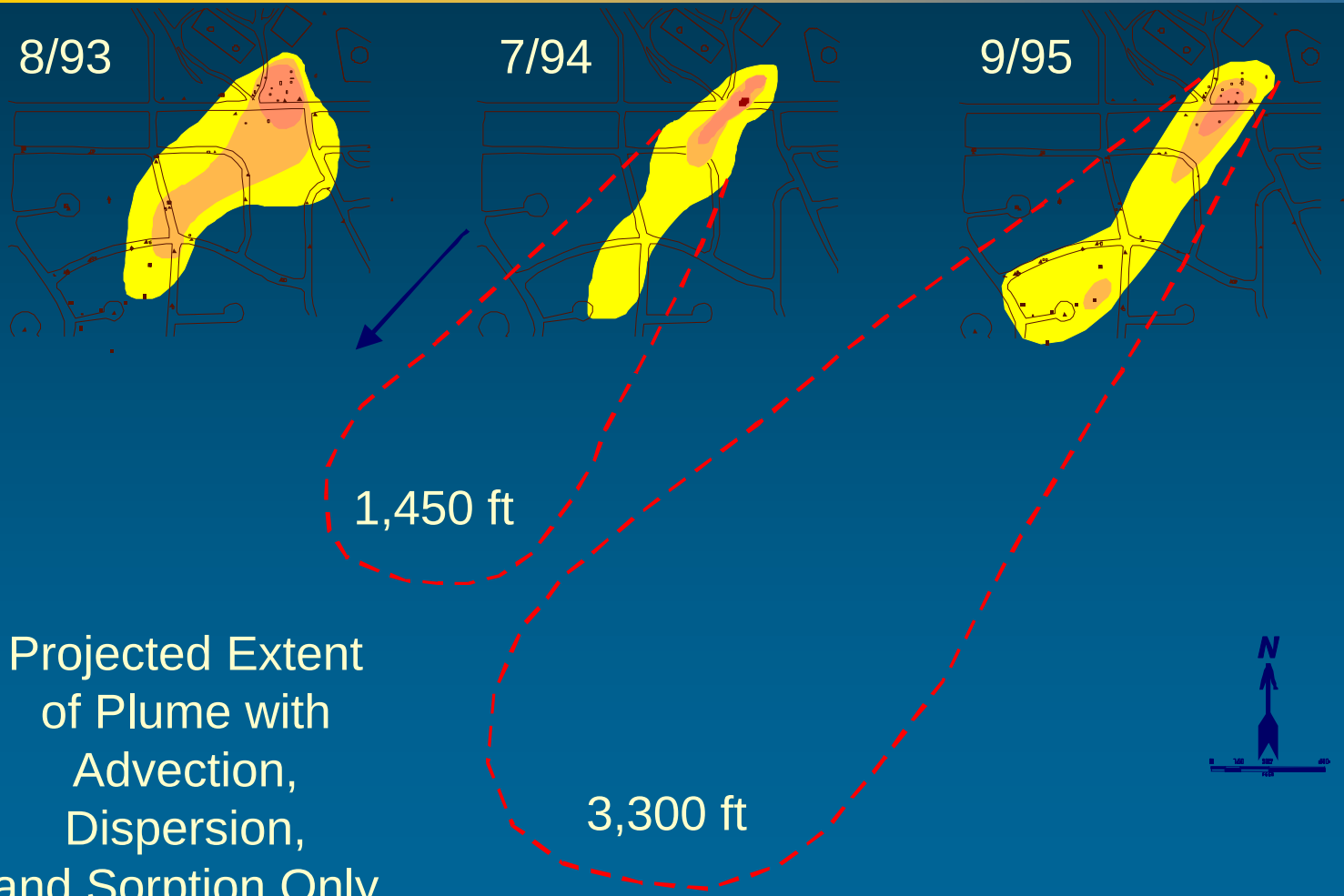
Documented Loss of Contaminant Mass at the Field Scale

- **Statistically Significant Historical Database Showing Plume Stabilization and/or Loss of Contaminant Mass Over Time**

Total BTEX - 8 feet of LNAPL



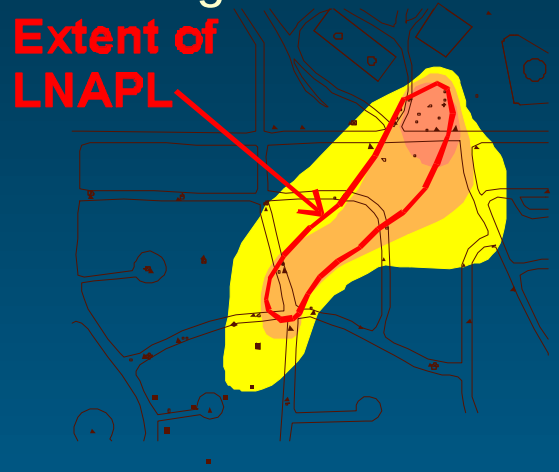
Total BTEX Projection



Projected Extent of Plume with Advection, Dispersion, and Sorption Only Biodegradation Omitted

Actual BTEX Migration vs. Time

August 1993

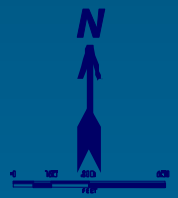


July 1994

Maximum Total BTEX Concentration on the Order of 15 mg/L Except 1994 (22 mg/L)

September 1995

September 1998

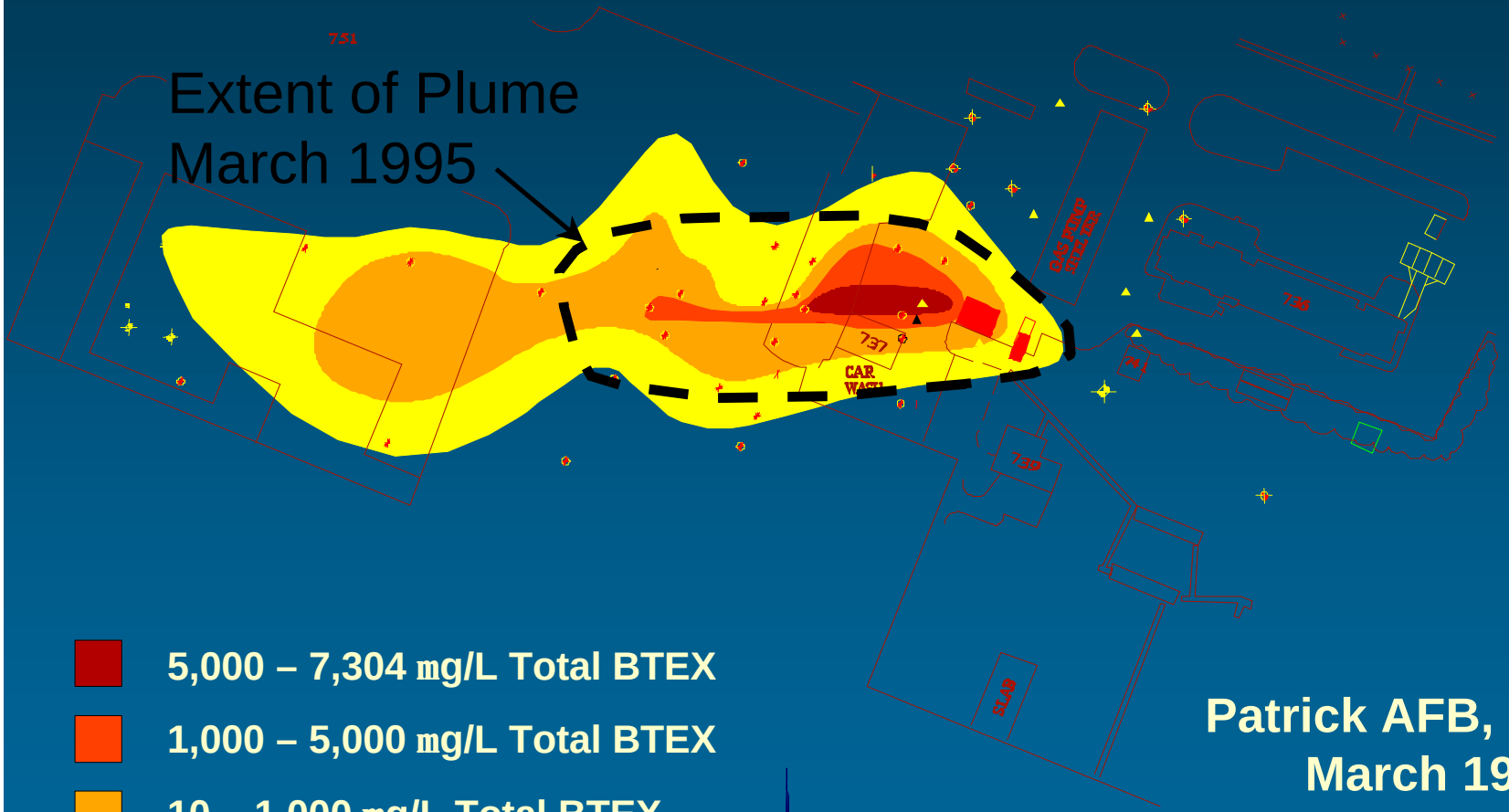


> 8,000 µg/L

4,000 - 8,000 µg/L

0 - 4,000 µg/L

Total BTEX in Groundwater - Source Removed



5,000 – 7,304 mg/L Total BTEX

1,000 – 5,000 mg/L Total BTEX

10 – 1,000 mg/L Total BTEX

0 – 10 mg/L Total BTEX

Patrick AFB, Florida
March 1994

Evaluating Plume Stability

- **Statistical Techniques Such As the Mann-Kendall Test Can Be Used To Check for Trends in Analytical Data and to Assess Plume Stability**

Relationship Between Contaminants and Geochemistry

- **Areas With Elevated Contaminant Concentrations Should/Will Show Elevated Metabolic Byproduct Concentrations and Depleted Electron Acceptor Concentrations**

Relationship Between Contaminants and Geochemistry

- **If Biodegradation is Occurring, Areas With Elevated Contaminant Concentrations Should Show**
  - **Depleted Dissolved Oxygen, Nitrate and Sulfate Concentrations**
  - **Elevated Fe(II), Methane, and Possibly Ethene/Ethane Concentrations**
  - **Lowered Oxidation/Reduction Potential**
  - **Elevated Chloride Concentrations**

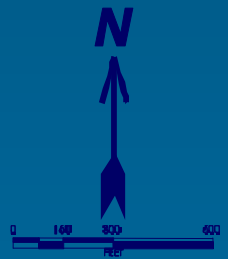
Example - Petroleum Hydrocarbon Contaminated Site

- **Site Contaminated With Petroleum Hydrocarbons**
- **Site Shows Evidence of:**
  - **Aerobic Respiration**
  - **Denitrification**
  - **Fe(III) Reduction**
  - **Sulfate Reduction**
  - **Methanogenesis**

Total BTEX

HILL AFB, JULY 1994

- 20,000 - 22,000 µg/L
- 8,000 - 20,000 µg/L
- 4,000 - 8,000 µg/L
- 0 - 4,000 µg/L



Dissolved Oxygen

HILL AFB, JULY 1994

- < 1 mg/L
- 1 - 3 mg/L
- 3 - 5 mg/L

Total BTEX and Dissolved Oxygen

HILL AFB, JULY 1994

- 20,000 - 22,000 µg/L
- 8,000 - 20,000 µg/L
- 4,000 - 8,000 µg/L
- 0 - 4,000 µg/L

1 — LINE OF EQUAL DISSOLVED OXYGEN CONCENTRATION (mg/L)

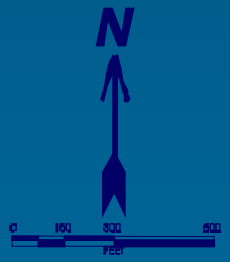
N

0 150 300 600
FEET

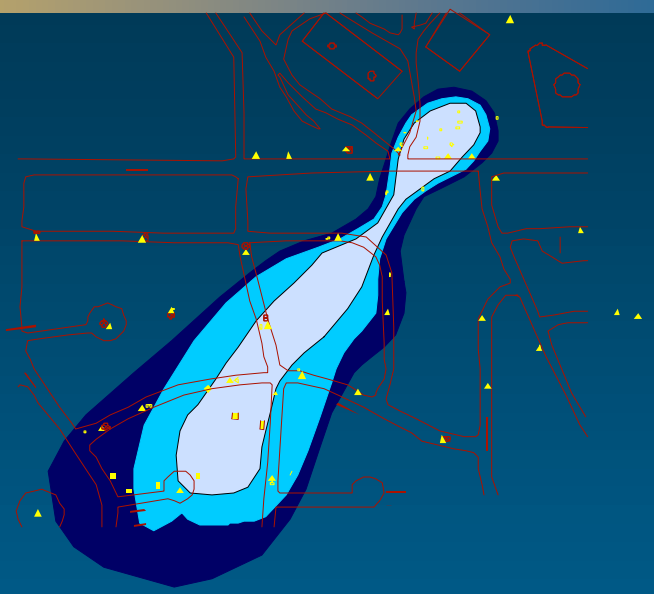
Total BTEX

HILL AFB, JULY 1994

- 20,000 - 22,000 µg/L
- 8,000 - 20,000 µg/L
- 4,000 - 8,000 µg/L
- 0 - 4,000 µg/L



Nitrate



HILL AFB, JULY 1994

- <0.05 mg/L
- 0.05 - 1 mg/L
- 1 - 5 mg/L

Total BTEX and Nitrate

HILL AFB, JULY 1994

- 20,000 - 22,000 µg/L
- 8,000 - 20,000 µg/L
- 4,000 - 8,000 µg/L
- 0 - 4,000 µg/L

5 Line of Equal Nitrate Concentration (mg/L)

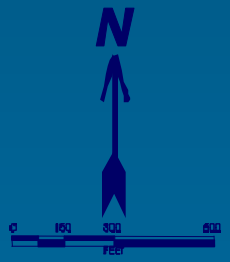
N

0 150 300 600
FEET

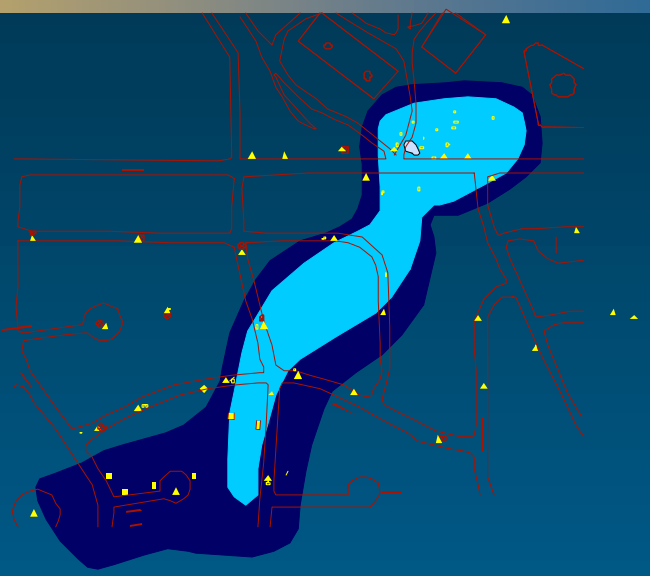
Total BTEX

HILL AFB, JULY 1994

- 20,000 - 22,000 µg/L
- 8,000 - 20,000 µg/L
- 4,000 - 8,000 µg/L
- 0 - 4,000 µg/L



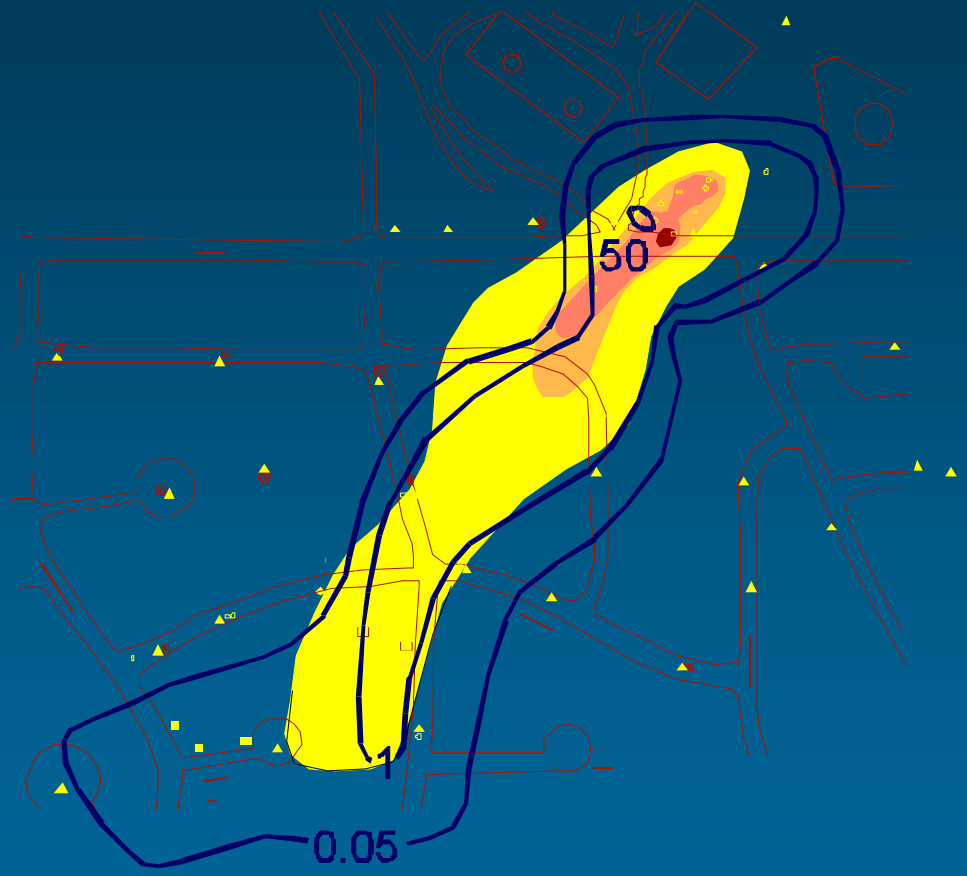
Fe(II)



HILL AFB, JULY 1994

- > 50 mg/L
- 1 -50 mg/L
- 0.05 - 1 mg/L

Total BTEX and Iron (II)



HILL AFB, JULY 1994

20,000 - 22,000 µg/L

8,000 - 20,000 µg/L

4,000 - 8,000 µg/L

0 - 4,000 µg/L

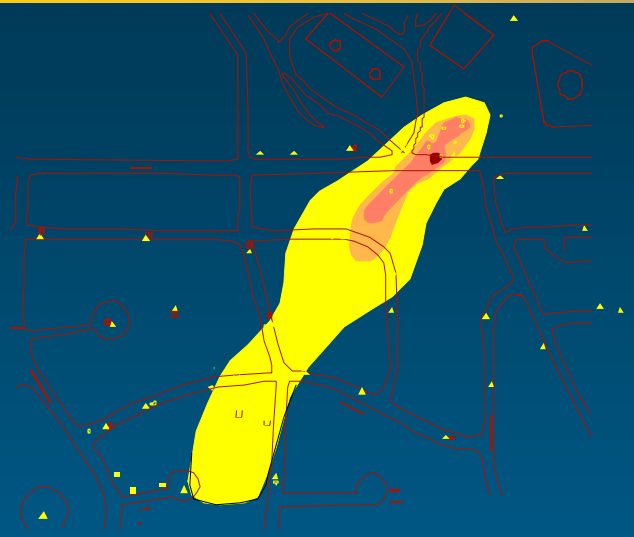
1 — LINE OF EQUAL IRON (II) CONCENTRATION (mg/L)

N

0 150 300 600

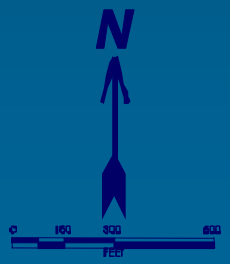
FEET

Total BTEX

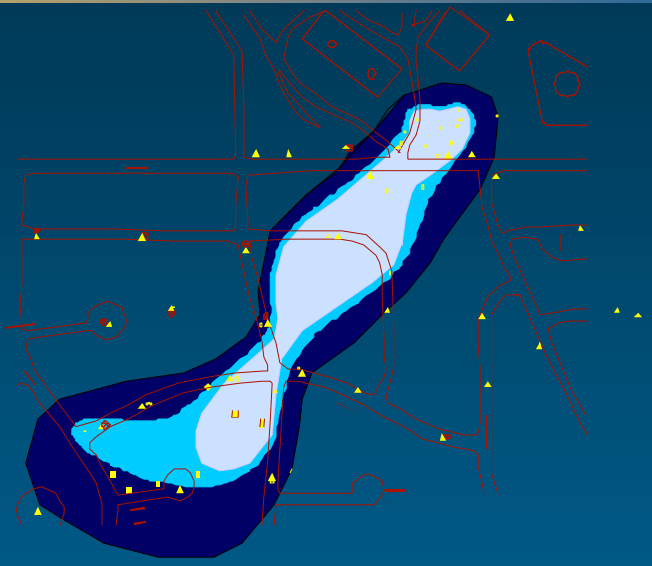


HILL AFB, JULY 1994

- 20,000 - 22,000 µg/L
- 8,000 - 20,000 µg/L
- 4,000 - 8,000 µg/L
- 0 - 4,000 µg/L



Sulfate



HILL AFB, JULY 1994

- <0.05 mg/L
- 0.05 - 40 mg/L
- 40 - 80 mg/L

Total BTEX and Sulfate

HILL AFB, JULY 1994

20,000 - 22,000 µg/L

8,000 - 20,000 µg/L

4,000 - 8,000 µg/L

0 - 4,000 µg/L

40 Line of Equal Sulfate Concentration (mg/L)

N

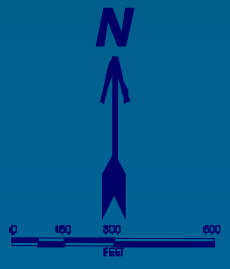
0 150 300 600

FEET

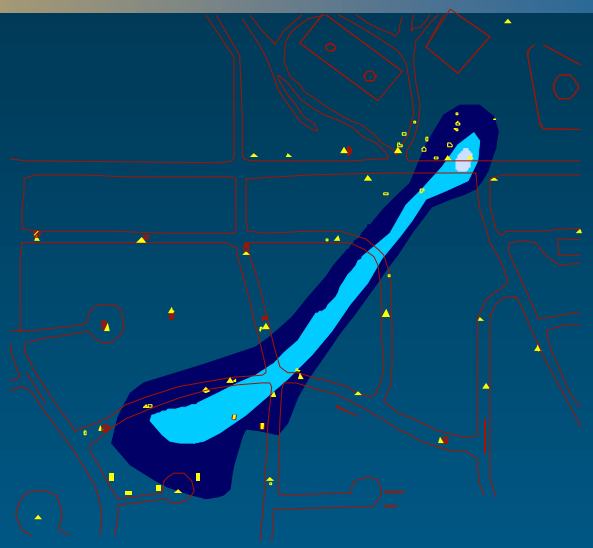
Total BTEX

HIII AFB, JULY 1994

- 20,000 - 22,000 µg/L
- 8,000 - 20,000 µg/L
- 4,000 - 8,000 µg/L
- 0 - 4,000 µg/L



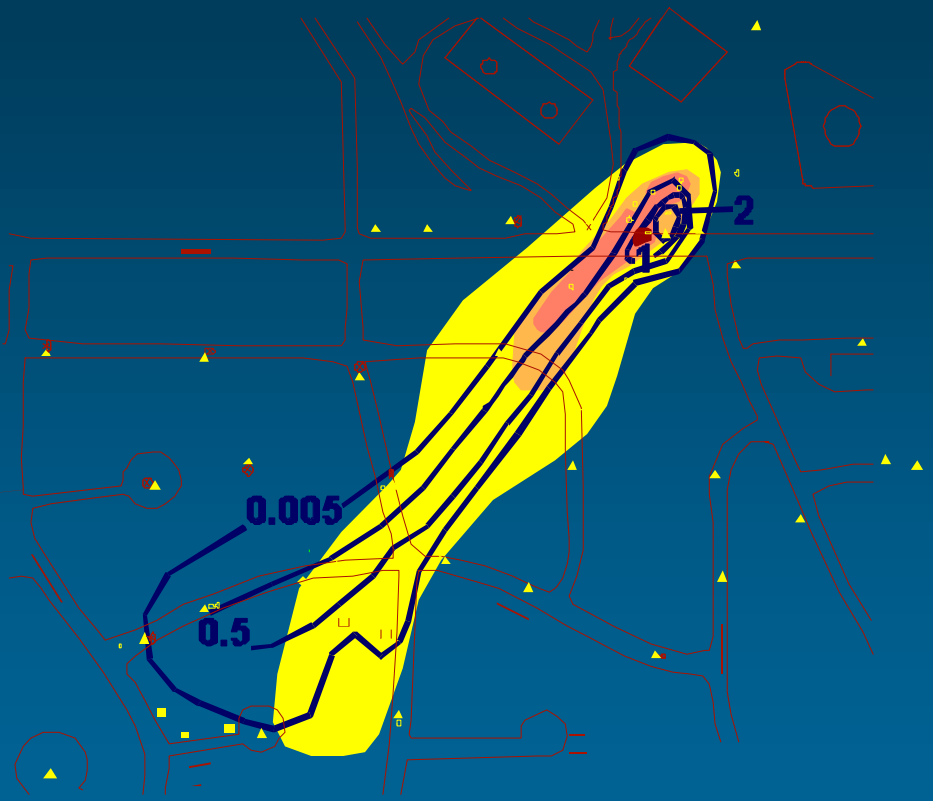
Methane



HILL AFB, JULY 1994

- >2 mg/L
- 0.05 - 2 mg/L
- 0.005 - 0.05 mg/L

Total BTEX and Methane



HILL AFB, JULY 1994

20,000 - 22,000 µg/L

8,000 - 20,000 µg/L

4,000 - 8,000 µg/L

0 - 4,000 µg/L

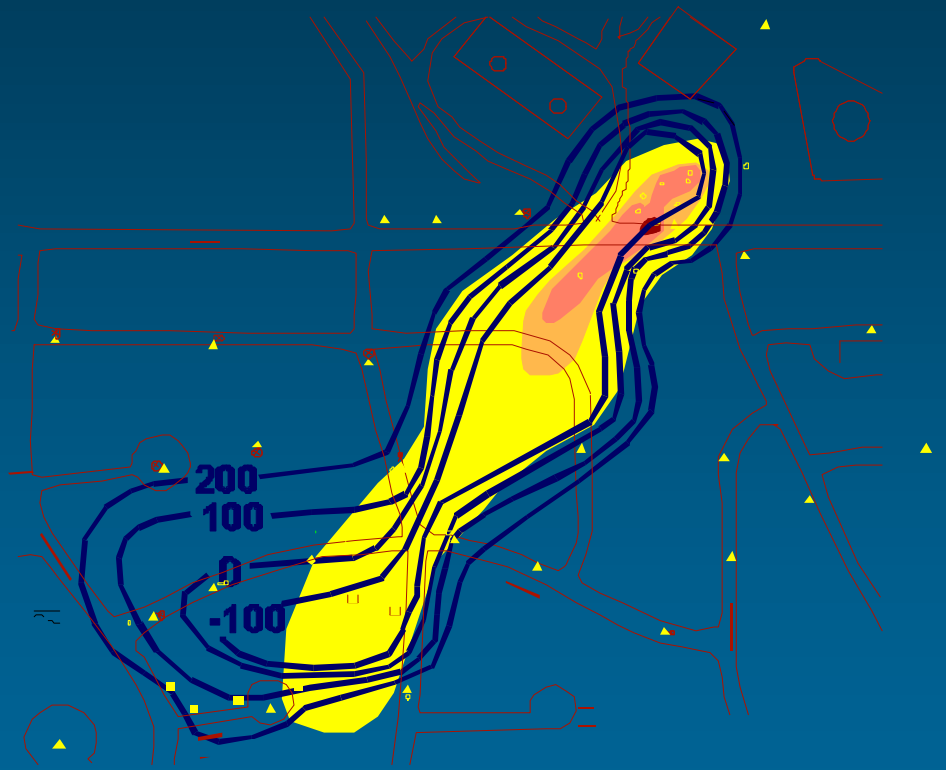
2 Line of Equal Methane Concentration (mg/L)

N

0 150 300 600

FEET

Total BTEX and Oxidation-Reduction Potential



HILL AFB, JULY 1994

20,000 - 22,000 µg/L

8,000 - 20,000 µg/L

4,000 - 8,000 µg/L

0 - 4,000 µg/L

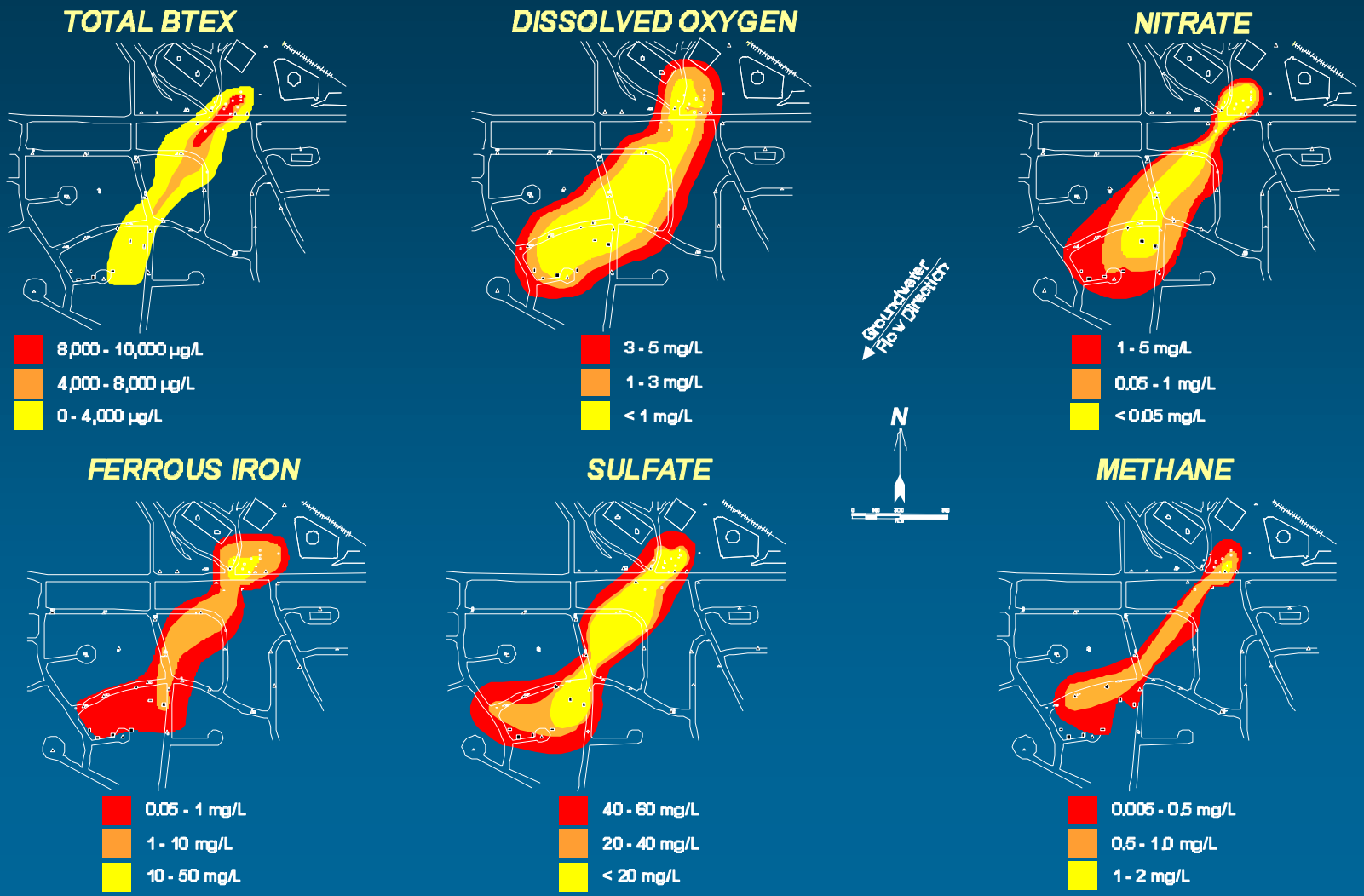
200 Line of Equal Oxidation - Reduction Potential (mV)

N

0 150 300 600

FEET

Summary of Geochemical Indicators of Biodegradation

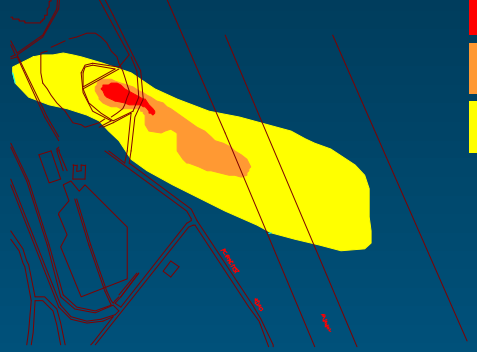


Example - Site Contaminated With Solvents and Fuel Hydrocarbons

- **Mixture of Chlorinated Solvents and Petroleum Hydrocarbons**
- **Site Shows Evidence of:**
  - **Aerobic Respiration, Denitrification, Fe(III) Reduction, Sulfate Reduction, and Methanogenesis**
  - **Reductive Dechlorination (Halorespiration)**

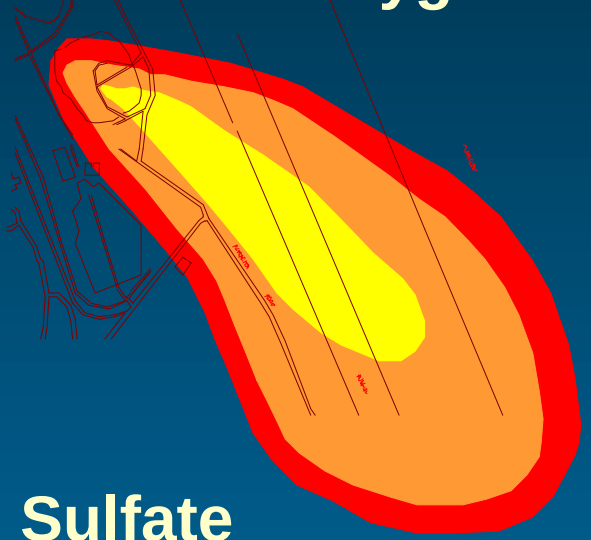
BTEX and Electron Acceptors

Total BTEX



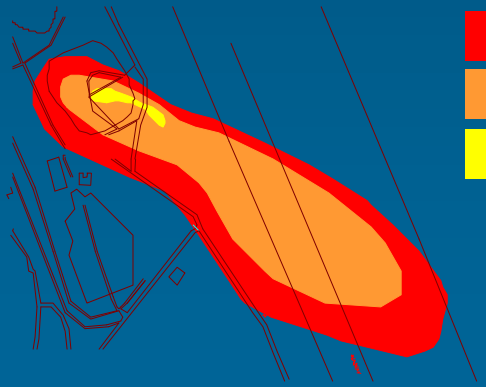
4,000 - 6,000 µg/L
2,000 - 4,000 µg/L
0 - 2,000 µg/L

Dissolved Oxygen



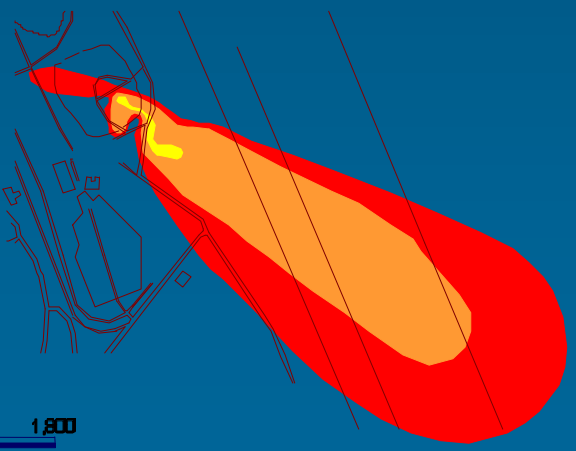
5 - 10 mg/L
1 - 5 mg/L
< 1 mg/L

Nitrate

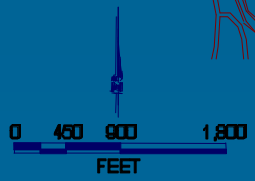


0.2 - 0.4 mg/L
0.05 - 2 mg/L
< 0.05 mg/L

Sulfate

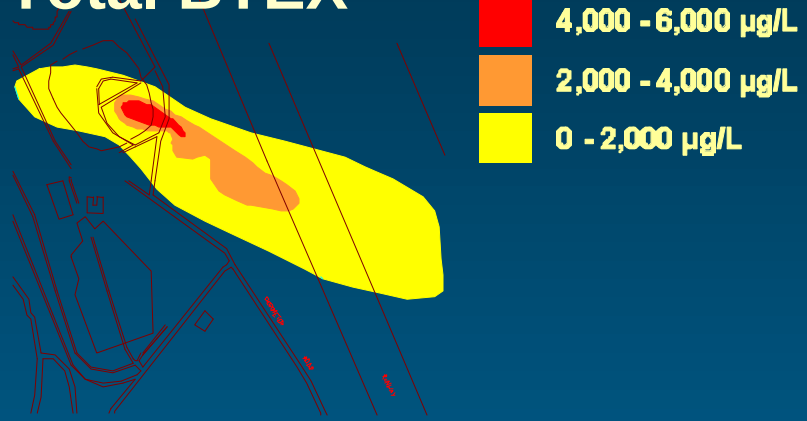


10 - 20 mg/L
0.05 - 10 mg/L
< 0.05 mg/L

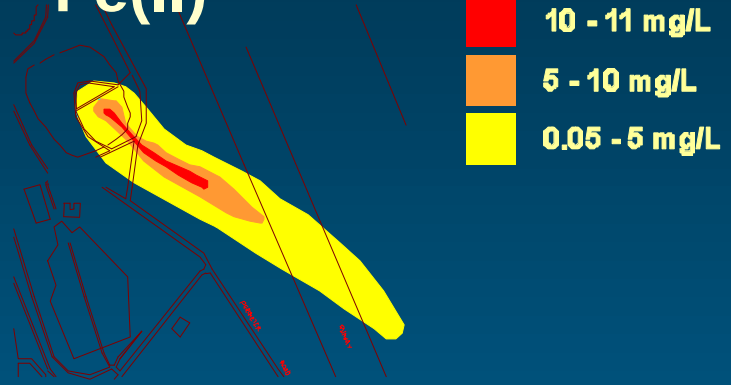


BTEX and Metabolic Byproducts

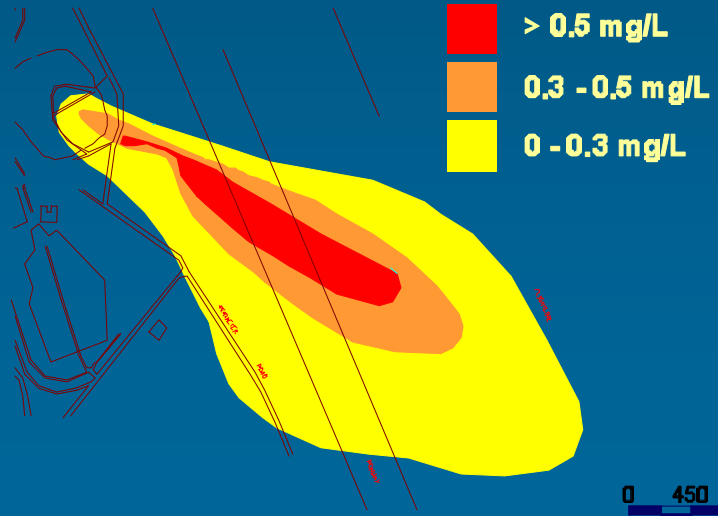
Total BTEX



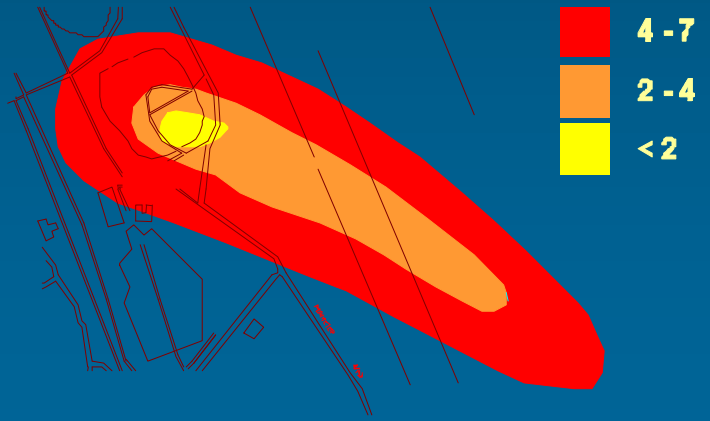
Fe(II)

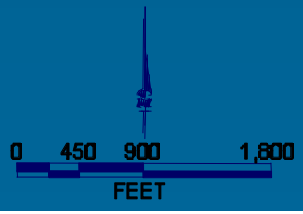


Methane



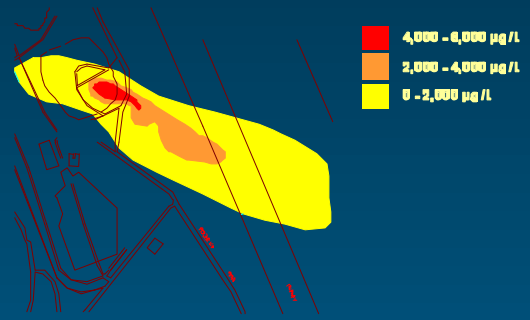
pE



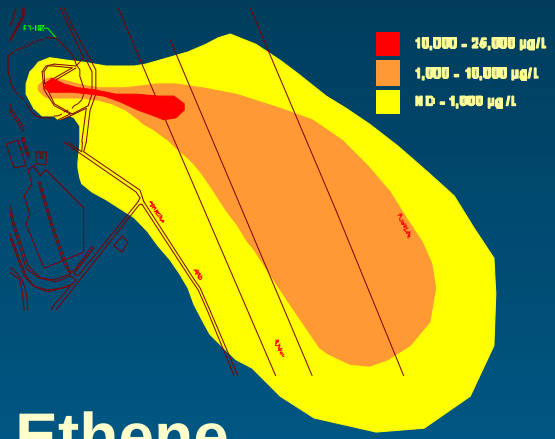


Chlorinated Solvents and Byproducts

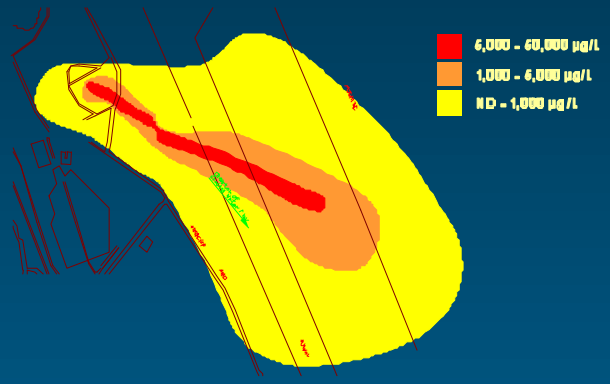
Total BTEX



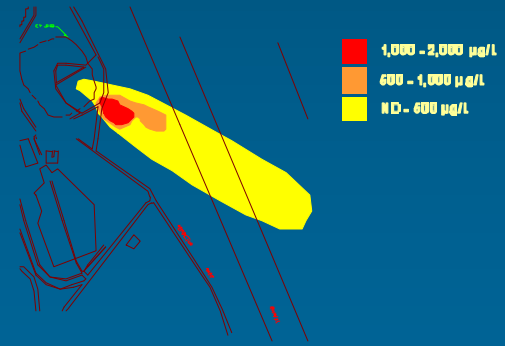
Trichloroethene



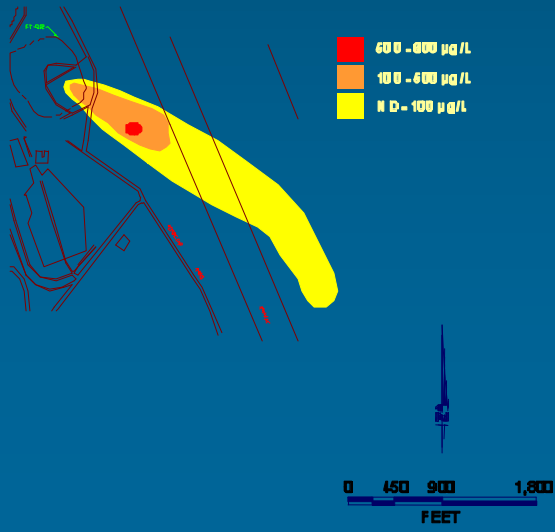
Dichloroethene



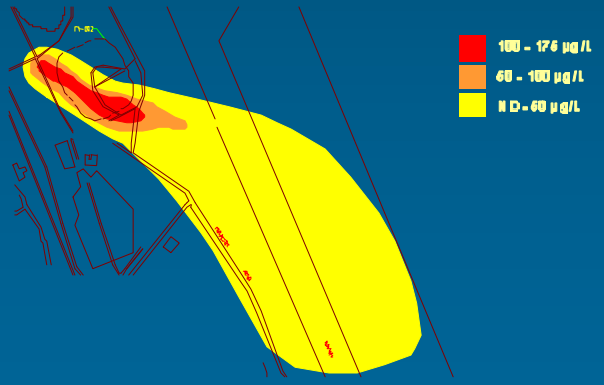
Vinyl Chloride



Ethene



Chloride



Trends During Biodegradation

Analyte	Upgradient (mg/L)	Plume Interior (mg/L)
Oxygen	11	<0.1
Nitrate	0.5	<0.05
Fe(II)	0.0	46
Sulfate	25	<0.05
Methane	<0.001	3.5
Chloride	2	82
Ethene	<0.001	0.182
Hydrogen	0.0	11nM

Additional Relationships

- **Maps Showing Trends in Alkalinity, Carbon Dioxide and Hydrogen Concentrations, etc. Also Can be Prepared**

Geochemical/Daughter Product Evidence of Natural Attenuation

- **Can Provide Very Convincing Evidence of Biodegradation**
- **May have Conflicting Data**
- **Weight of Evidence is a Must**

Microbiological Laboratory Evidence

- **Should Be Used Very Selectively In Accessing Natural Biodegradation**
- **Should Only Be Used When A Process Is Not Understood**
- **Example - DCE Oxidation**

Problems With Microcosms

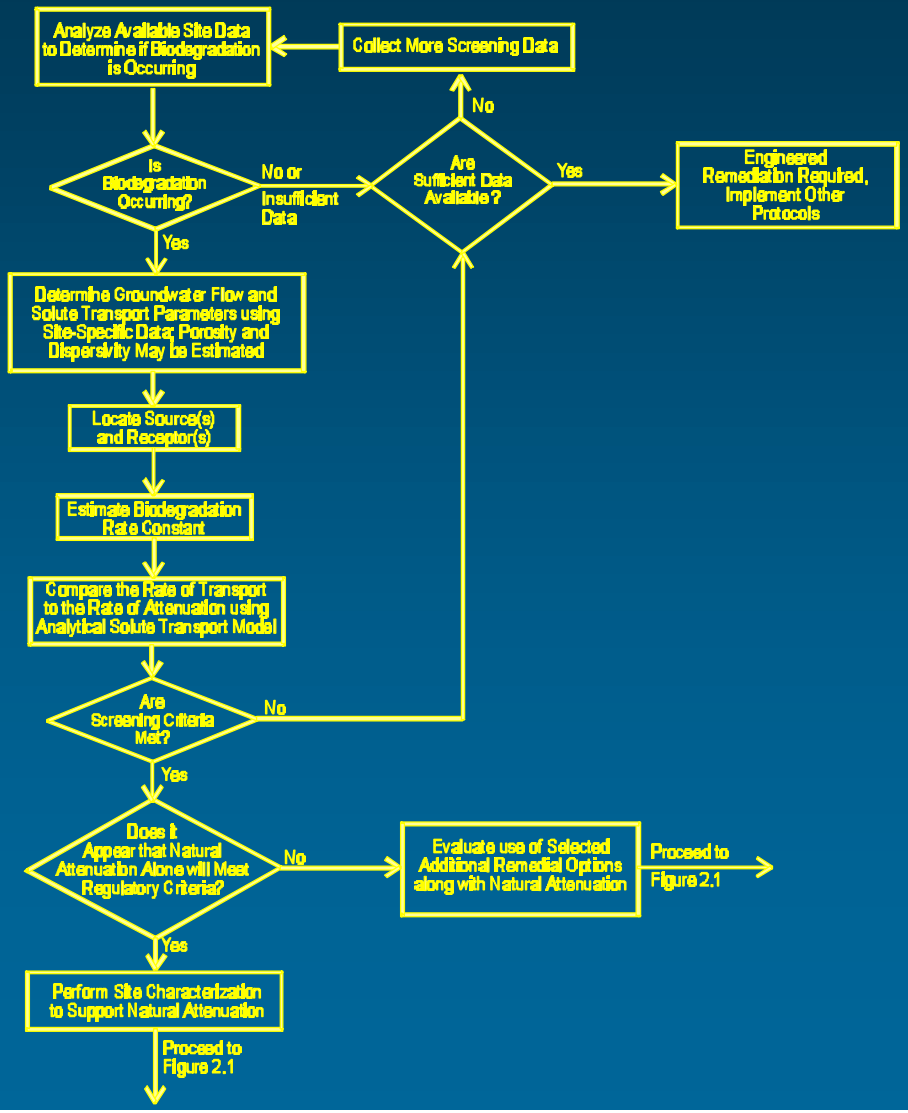
- **Laboratory Findings Cannot be Translated Directly to Field Settings**
- **Anaerobic Biodegradation of Contaminants Results From the Interactions of a Microbial Consortia**
- **Removing Aquifer Material From Its Original Setting Disrupts the Balance of the Consortia, Which in Turn Inhibits Biodegradation**

Screening for Biodegradation (Dehalorespiration) of Solvents

- **Actual AFCEE/EPA Screening Processes is More Detailed**
- **See EPA/600/R-98/128, Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water**

  ftp://ftp.epa.gov.pub/ada/reports/protocol.pdf

Initial Screening Process Flow Chart



Screening Steps

1 Determine if Biodegradation (Halorespiration) is Occurring

2 Determine Groundwater Flow and Solute Transport Parameters

3 Locate Sources and Receptor Exposure Points

4 Estimate Biodegradation Rates

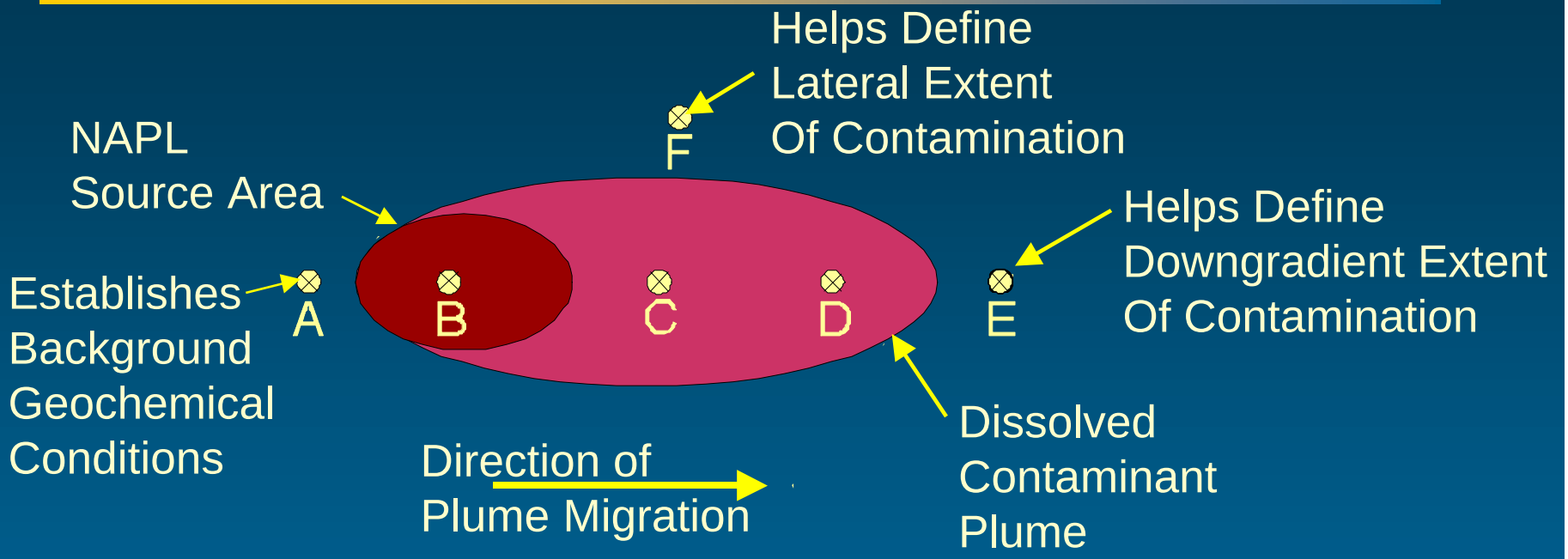
5 Compare Rate of Transport to Rate of Attenuation

6 Determine if Screening Criteria are Met

Screening for Biodegradation (Dehalorespiration) of Solvents

- **Screening for Reductive Dechlorination Consists of Collecting Samples Inside the Contaminant Plume**

Data Collection Points for Initial Screening



LEGEND

- Required Data Collection Point
  Not to Scale

Use Data from Points B and C for Biodegradation Screening

Analyze Samples For:

- VOC Analysis (8260)
- Dissolved Oxygen
- Nitrate/Nitrite
- Fe(II)
- Sulfate/Sulfide
- Methane/Ethane/ Ethene
- Chloride
- Carbon Dioxide
- Hydrogen (Optional)
- Total Organic Carbon
- Redox Potential
- Alkalinity
- pH
- Temperature

Determine if Reductive Dechlorination is Likely Occurring

- **Use Analytical Parameter Weighting System to Determine if Biodegradation (Dehalorespiration) is Likely Occurring**

- **Different Portions of the Plume May Exhibit Differing Behavior**
  - **e.g. Type 1 Environment Near Source with Type 3 Conditions Downgradient**

Analytical Parameter Weighting

Analysis	Concentration in Plume	Value
Oxygen	<0.5 mg/L	3
	>5 mg/L	-3
Nitrate	<1 mg/L	2
Fe(II)	>1 mg/L	3
Sulfate	<20 mg/L	2
Methane	<0.5 mg/L	0
	>0.5 mg/L	3
ORP	<50mV	1
	<-100mV	2

Analytical Parameter Weighting

Analysis	Concentration in Plume	Value
pH	5< pH <9	0
	5> pH >9	-2
TOC	>20 mg/L	2
Temperature	>20^{o}C	1
CO_2	>2X Background	1
Alkalinity	>2X Background	1
Chloride	>2X Background	2
Hydrogen	<1 nM	0
	>1 nM	3

Analytical Parameter Weighting

Analyte	Concentration in Plume	Value
BTEX	>0.1 mg/L	2
PCE	Spilled	0
TCE	Spilled	0
	Daughter Product	2
DCE	Spilled	0
	Daughter Product	2
VC	Spilled	0
	Daughter Product	2
Ethene/Ethane	>0.01 mg/L	2
	>0.1 mg/L	3

Analytical Parameter Weighting

Analyte	Concentration in Plume	Points Awarded
1,1,1 TCA	Spilled	0
DCA	Spilled	0
	Daughter Product	2
Chloroethane	Spilled	0
	Daughter Product	2
Carbon Tetrachloride	Spilled	0
	Daughter Product	2
Chloroform	Spilled	0
	Daughter Product	2
Dichloromethane	Spilled	0
	Daughter Product	2

Analytical Parameter Weighting

Analyte	Concentration in Plume	Value
Hexachlorobenzene	Spilled	0
Pentachlorobenzene	Spilled	0
	Daughter Product	2
Tetrachlorobenzene	Spilled	0
	Daughter Product	2
Trichlorobenzene	Spilled	0
	Daughter Product	2
Dichlorobenzene	Spilled	0
	Daughter Product	2
Monochlorobenzene	Spilled	0
	Daughter Product	2

Interpretation of Points Awarded During Screening

Score	Interpretation
0 to 5	Inadequate Evidence for Reductive Dechlorination of Chlorinated Solvents
6 to 14	Limited Evidence for Reductive Dechlorination of Chlorinated Solvents
15 to 20	Adequate Evidence for Reductive Dechlorination of Chlorinated Solvents
> 20	Strong Evidence for Reductive Dechlorination of Chlorinated Solvents

Strong Evidence for Reductive Dechlorination

Analyte	Concentration in Plume	Points Awarded
Oxygen	0.1 mg/L	3
Nitrate	0.3 mg/L	2
Fe(II)	10 mg/L	3
Sulfate	2 mg/L	2
Methane	10 mg/L	3
ORP	-190 mV	2
Chloride	3 times background	2
PCE (released)	1,000 µg/L	0
TCE (non released)	1,200 µg/L	2
cis-DCE (non released)	2,500 µg/L	2
VC (non released)	5,000 µg/L	2
	Total	23

Inadequate Evidence for Biodegradation

Analyte	Concentration in Plume	Points Awarded
Oxygen	8 mg/L	-3
Nitrate	0.3 mg/L	2
Fe(II)	ND	0
Sulfate	10 mg/L	2
Methane	ND	0
ORP	100 mV	0
Chloride	background	0
PCE (released)	1,000 µg/L	0
TCE (non released)	ND	0
cis-DCE (non released)	ND	0
VC (non released)	ND	0
	Total	1

Limitations of the Screening Method

- **Just Because You Pass the Screening Does NOT Mean that Natural Attenuation Will Work**
- **It Only Means it MAY Work!!**
- **Further Investigation is Required**

Using Models to Evaluate Natural Attenuation

- **Although not a Line of Evidence Analytical or Numerical Models can Prove Valuable for Evaluating Natural Attenuation**

Using Models to Evaluate Natural Attenuation

- **Dominant Transport Mechanisms at Many Sites Include**
  - **Advection**
  - **Dispersion**
  - **Sorption**
  - **Biodegradation**

Using Models to Evaluate Natural Attenuation

- **Models can be used to Evaluate the Relative Importance of Natural Attenuation Mechanisms**

Using Models to Compare Active Remediation to Natural Attenuation

- **A Groundwater Flow and Solute Transport Model was used to Compare the Effectiveness of Natural Attenuation to Several Remedial Alternatives**
- **Modflow Coupled to ModflowT**

Using Models to Compare Active Remediation to Natural Attenuation

- **Complex Model**
  - **x = 29,040 feet**
  - **y = 16,500 feet**
  - **z = variable but on the order of 200 feet**
  - **21 layers**
  - **369,600 grid blocks!**

Using Models to Compare Active Remediation to Natural Attenuation

- **Natural Attenuation was Compared to 7 Extraction, Treatment, and Reinjection (ETR) Scenarios**

- **Some Very Interesting Things Came to Light**

Using Models to Compare Active Remediation to Natural Attenuation

Alternative	Total VOC Mass Remaining in Modeled Subsurface (kg)						Cost (Millions)
	1998	2008	2018	2028	2038	2048	
2 – MNA	2,635	1,404	651	277	120	55.9	3
3A – ETR (ALTERNATIVE E)	2,635	1,186	434	133	37.1	10.4	160
3B – ETR (MODIFIED E)	2,635	1,058	376	130	46.3	17.4	120
3C – ETR (EPA)	2,635	1,054	375	130	45.4	16.3	106
3D – ETR (Cataumet)	2,635	1,300	571	235	97.2	42.8	40
3E – ETR (Warm Spots)	2,635	1,087	399	140	53.2	21.4	71
4A – Protection of Bourne Wells (ETR Modified 3B)	2,635	1,321	596	261	116	54.8	45
4B – Protection of Bourne Wells (ETR)	2,635	1,372	615	249	102	46.3	62

Using Models to Compare Active Remediation to Natural Attenuation

Alternative	Peak Total VOC Aquifer Concentration (mg/L)	
	2018	2048
2 – MNA	52.7	7.8
3A – ETR (Alternative E)	53.1	3.2
3B – ETR (Modified E)	43.6	3.1
3C – ETR (EPA)	52.7	2.7
3D – ETR (Cataumet)	53.3	5.1
3E – ETR (Warm Spots)	52.9	5.2
4A – Protection of Bourne Wells (ETR Modified 3B)	41.8	6.2
4B – Protection of Bourne Wells (ETR)	52.8	7.0

Using Models to Compare Active Remediation to Natural Attenuation

Remedial Alternative	Mass Removed Over Natural Attenuation After 50 years (Kg)	Total Remediation System Cost (dollars)	Cost per Additional Kilogram Removed
MNA	0	3,000,000	0
3A	46	160,000,000	$3,500,000/Kg
3B	39	120,000,000	$3,000,000/Kg
3C	40	106,000,000	$2,650,000/Kg
3D	13	40,000,000	$3,000,000/Kg
3E	35	71,000,000	$2,000,000/Kg
4A	1	45,000,000	$45,000,000/Kg
4B	10	62,000,0000	$6,200,000/Kg

Using Models to Compare Active Remediation to Natural Attenuation

- **All of the ERT Systems were Extremely Expensive and Did Almost Nothing to Remediate the Aquifer**
- **In Addition, The ERT Systems did not Afford any Additional Protection of Human Health and the Environment**
- **In Fact, Many of the ERT Systems had Detrimental Environmental Impacts**